

Millimeter and Submillimeter Spectroscopy of Chlorine Nitrate: The Cl Quadrupole Tensor and the Harmonic Force Field¹

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Abstract

The rotational spectra of $^{35}\text{ClONO}_2$ and $^{37}\text{ClONO}_2$ in their ground and first excited torsional states ($\nu_9 = 1$) have been reinvestigated in selected regions between 84 and 441 GHz. An extensive set of spectroscopic constants has been determined, enabling more accurate predictions of line positions in the submillimeter region. Accidental near-degeneracies of rotational levels cause perturbations of the quadruple patterns, allow the observation of a $\Delta J = 2$ transition, and result in the precise determination of χ_{ab} . The quartic distortion constants along with the vibrational wavenumbers and inertial defect differences have been used for a calculation of the harmonic force field. The assignment of the vibrational modes in terms of internal coordinates is discussed. The results are compared with properties of related molecules such as Cl_2O .

1. INTRODUCTION

Chlorine nitrate, ClONO_2 , has been known for more than 40 years (1). It has attracted considerable interest as an important temporary reservoir species in stratospheric chemistry. Particularly in the polar vortex, the formation of ClONO_2 from ClO and NO_2 removes substantial amounts of reactive chlorine and nitrogen species from catalytic cycles of ozone destruction. Reactions of ClONO_2 on the surfaces of polar stratospheric cloud particles and the subsequent photolysis of the products release reactive chlorine atoms which lead, for example, to the ozone hole observed over Antarctica (2). Therefore, most of the large number of studies on chlorine nitrate were initiated in order to better understand its role in stratospheric chemistry. These studies include microwave (3, 4) and millimeterwave spectroscopic investigations (5) in the ground and first excited torsional state ($v_9 \approx 1$) as well as infrared (IR) studies in the gas phase (e. g. 6 - 9) and in matrix (e. g. 10, 11). The ν_4 and ν_5 vibrational bands have been used to evaluate column densities of stratospheric ClONO_2 (e. g. 12). Temperature dependent absorption cross sections have been studied to enable a precise quantification of the compound. More recently, the rotational structures of the ν_4 (13) and ν_2 band (14) have been resolved and analyzed using diode laser spectroscopy of jet-cooled samples. Recently, the molecular structure in the gas phase has been revealed by means of electron diffraction (15).

The primary aim of the present study was to examine the bonding of ClONO_2 , particularly of the ClO bond. One tool used has been the analysis of the Cl quadrupole tensor in terms of ionic- and π -bonding. Further information, not only on the bonding in this molecule, but also on the description of the normal modes in terms of internal coordinates, has been gained from a calculation of the harmonic force field.

A further aim of this work was to provide more precise spectroscopic constants of ClONO_2 in the ground and first excited torsional states which should be useful for the analysis and simulation of vibrational bands, for the study of rotational spectra of other excited vibrational states, and for the detection of stratospheric ClONO_2 by means of millimeter or submillimeter spectroscopy, once the instrumental sensitivity is sufficient for this purpose.

11. EXPERIMENTAL

The methods used for the synthesis of chlorine nitrate were taken from Ref. (16). At JJ', the ClONO_2 was obtained from the reaction of Cl_2O and N_2O_5 . The latter compounds were synthesized from $\text{Cl}_2 + \text{HgO}$ and $\text{NO}_2 + \text{O}_3$ respectively.

The measurements were done employing a 1 m long free space, double-path glass cell. Phase-locked klystrons (Varian) were used as sources, either on fundamental frequencies (*ca.* 84-119 GHz) with a diode detector, or at third or fourth harmonic (*ca.* 369-441 GHz) using harmonic generators and a liquid He.-cooled InSb hot electron bolometer as detector. Further details of the spectrometer system are given elsewhere (17). Measurements were carried out in a slow flow mode at room temperature with the sample container held at *ca.* -110°C. The pressure in the cell was adjusted to ~0.05 - 2 Pa (~0.4 - 15 mTorr) depending on the strengths of the lines and the intended resolution.

At South Alabama, the chlorine nitrate sample was synthesized through the reaction of anhydrous nitric acid with chlorine monofluoride (16). Measurements were made in the 200 GHz region with a microwave source consisting of a phase-locked OK124V10 klystron driving a harmonic multi-

plier of the King Gordy design (18); an InSb hot electron bolometer operated at liquid helium temperatures was used as the detector. The absorption cell was a 2-cm ID stainless steel tube, 3-m in length, and was held at room temperature.

11.1. Observed Spectra and Analysis

Chlorine nitrate is a planar, slightly asymmetric prolate rotor ($\kappa \approx -0.90$) with a moderate dipole component along the a -axis ($\mu_a = 0.72$ (7) D) and a smaller b -component ($\mu_b = 0.28$ (2) D) (4). Because of the relatively small rotational constants and several low lying vibrational states its pure rotational spectrum is rather rich. At room temperature the a -type R-branches are the strongest features even at 450 GHz ($80 \leq J \leq 100$). This type of transition was mostly well predicted from previous measurements (3-5) up to ca. 200 GHz. The b -type lines were considerably weaker, particularly Q- and P-branch transitions, and they were not as well predicted, mainly because of the limited precision of D_K and χ ($:= \chi_{bb} - \chi_{cc}$). Newly observed transitions improved the predictions, and the quadrupole patterns were helpful for the assignments, particularly for very weak, rather high K_a b -type transitions for which splittings were strongly influenced by χ .

The observed lines around 100 GHz consisted mainly of b -type transitions. Some a -type lines were observed as well, mainly for $^{37}\text{ClONO}_2$, both in the ground and first excited torsional state. Around 200 GHz higher K_a a -type R-branch transitions were recorded along with lower K_a a - and some b -type R-branch transitions. Around 400 GHz a -type R-branch lines were observed, as well as some high K_a b -type lines.

The z-quadrupole axis is expected to be close to the ClO bond which is not aligned with a principal inertial axis. Therefore, the Cl quadrupole tensor is incompletely described by its diagonal elements. Effects of the off-diagonal quadrupole coupling constant χ_{ab} are only manifest in perturbations of the quadrupole patterns of near-degenerate rotational levels with $\Delta J \leq 2$, $\Delta K_a = 1$, and ΔK_c even. The rotational constants and the expected magnitude of χ_{ab} of ClONO₂ are such that only few levels get close enough to observe large effects in the frequency regions of the spectrometers used, See Table 1.

The largest effect is seen for ³⁵ClONO₂ in the ground vibration] state. The experimental spectrum deviates substantially from the one calculated without χ_{ab} , see Fig 1. In this figure it has also been shown that of the two rotational transitions two lines each are essentially unperturbed, whereas two are shifted by up to *ca.* 4 MHz. The unperturbed levels 24_{6,18} and 23_{7,16} are less than 43 MHz apart, as can be seen from a detail of the energy level diagram (Fig. 2). Only sublevels with the same *J'* quantum number can interact. Because $\Delta J = J$, one sublevel can be unaffected in the absence of other perturbations.

The degree of perturbation can also be taken as an indication of the degree of mixing. Accordingly, it was possible not only to observe transition from the 22_{7,15} level to 23_{7,16}, but also to 24_{6,18}, see Fig. 3. As expected, the *J'* = 24.5 hyperfine component is much stronger than the *J'* = 22.5 component; but both are much weaker than the components of the formally allowed transition.

Both isotopomers and both vibrational states were fit simultaneously in a global non-linear, least-squares fit using Pickett's SPFIT/SPCAT program suite (19). Individual constants were used throughout, except for the sextic centrifugal distortion constants. Common sextic constants were used. In addition, for H_J , H_{JK} , and H_{KJ} changes from ³⁵ClONO₂ to ³⁷ClONO₂ and from the ground to

the excited torsional state were used; both the χ_{aa} changes with their uncertainties were applied to $^{37}\text{ClONO}_2$, $v_9 = 1$. Previously reported microwave and millimeterwave lines (4, S) were also used in the fit. Lines which had residuals larger than four times the estimated uncertainties were eliminated from the final fit; a different rejection threshold (\geq three times the estimated uncertainties) affected the parameters in general within their quoted uncertainties. The uncertainties were also little changed, with the exception of those for χ_{aa} because of relatively large residuals of some early reported low J microwave lines with rather large quadrupole splittings.

The newly observed lines are given in Table 2. In order to minimize the size of the table, the J' quantum number assignments are given relative to J ; because $\Delta J = \Delta J'$ between lower and upper state, one value of $J' - J$ is sufficient for an unambiguous assignment, except for the $\Delta J = 2$ transition, in the case of prolate or oblate pairing of rotational transitions K_c or K_a , respectively, has been omitted. The complete line list and predictions for the ground vibrational state are available on-line from the JPL spectral line catalogue at <http://spect.jpl.nasa.gov> or by anonymous ftp at [spec.jpl.nasa.gov](ftp://spec.jpl.nasa.gov). The spectroscopic constants are in Table 3; even though Watson's S-reduction is the preferred one for a rather symmetric rotor like ClONO_2 , results for the A-reduction are also included. Quadrupole coupling constants and derived parameters for $^{35}\text{ClONO}_2$ in the ground vibrational state are given in Table 4 together with values for the related molecules Cl_2O and ClH .

The present spectroscopic constants are more precise than the previous ones or have been determined for the first time. They allow predictions of lines into the submillimeter region. The uncertainties for strong or moderately strong lines are expected to be less than 1 MHz unless $K_a \gg 15$ for b-type lines or $J \gg 100$. The increased precision of the quartic distortion constants, particularly D_K , were useful for the force field calculation; and they also provided accurate predictions of energy

levels up to moderately high J and K_a quantum numbers, important to determine χ_{ab} precisely.

The inertial defect differences of the ν_4 band (13) were intended to be used in the force field calculation. Using the present groundstate constants, it was found that the observed lines could be fit with the same standard deviation as in (13) when only band centers and changes in the rotational constants were used. The derived constants are in Table 5. The present constants agree in general within cmc standard deviation with those of Ref. (13). They are suggested to be more accurate because fewer constants were needed.

1 V. THE CL QUADRUPOLE TENSOR

1 Diagonalization of the quadrupole tensor reveals that it is rather symmetric around the principal z-axis and that the absolute value of the coupling constant along this axis is only slightly larger than in Cl_2 : -111.8 (2.?). Using methods outlined elsewhere (24), one derives rather small contributions from the ionic form $\text{Cl}^+\text{ONO}_2^-$ and from z-bonding, cf. Table 4. The principal quadrupole coupling constants and derived parameters of ClONO_2 are very similar to those of Cl_2O , see Table 3; even though χ_{ab} of Cl_2O was determined for the $V_2 = 2$ state only (22), and its precision may be limited, the effect on the derived parameters is suggested to be small. The rather small ionic contributions to the ClO bonds in ClONO_2 and Cl_2O are compatible with the view that the OX group in general is only slightly more electronegative than the Cl atom.

It is interesting to note that the z-quadrupole axes in ClONO_2 and Cl_2O deviate from the ClO bond by a similar amount: 2.75° and 2.4° respectively, cf. Fig. 4. Although these deviations are small

they are important for estimating the ClO bond character. For example in the case of Cl_2O , χ_{ab} was not known initially, and the z-axis was assumed to be collinear to the ClO bond; ionic- and π -characters of 0.35 and 0.09, respectively, were derived for the ClO bond in Cl_2O (21). If one would assume in the same way the z-axis in ClONO_2 to be aligned with the ClO bond one would derive for example an ionic character of about 0.31, similar to that of the ClF bond in that molecule. This would be in contrast to the view that the F atom in general is much more electronegative than the OX group. This type of deviation between a principal quadrupole axis and a molecular bond is found rather frequently and has often led to wrong estimates of ionic- or π -contributions; see also the investigation of SOCl_2 in Ref. (2.5).

V. THE HARMONIC FORCE FIELD

(a) Calculation

A normal coordinate analysis was undertaken in order to characterize the bonding in ClONO_2 and to obtain (expressions of the normal modes in terms of internal coordinates. The computation of the general valence force field was carried out with Christen's program NCA (26). Because there are redundant coordinates in ClONO_2 , the choice of internal coordinates is not straightforward. In the NCA program the calculation is performed in Cartesian coordinates, and it is allowed to use redundant coordinates. Since this would lead to a solution space with a dimension larger than 0 (no unique solution exists even theoretically), the number of coordinates was constrained to 9: the ClO, ON, NO_2 ,

and NO_2 bonds and the ClON , ONO_e , and ONO_i angles which are only related to vibrations in a' , see also Fig. 4; the ONO_2 out-of-plane coordinate, (oop), and the torsion τ of the Cl , O_e , and O_i atoms around the, ON bond, which are related to vibrations in a'' . The r_s structure of Ref. (5) was taken to describe the molecular geometry. The initial force constants were taken from an *ab initio* calculation (27) adjusted for the change in coordinates.

For the force field calculation several different types of input data have been taken into account. The relative weights among the same type of input data (e.g. the quartic distortion constants) were mostly inversely proportional to the squares of the experimental uncertainties. Among the different types the relative uncertainties were chosen to ensure that each type of data is well reproduced with respect to the uncertainties.

The ground state quartic distortion constants in the A-reduction from this study were used with ten times the experimental uncertainties; the S-reduction is not implemented in the present N(7A) version. Band positions of the fundamentals (0.1 cm^{-1} uncertainty) and $^{35/37}\text{Cl}$ isotopic shifts (0.01 cm^{-1} unc.) for ν_3 and ν_5 (9), ν_4 (13), and ν_6 (8), as well as fundamentals of ν_1 and ν_8 (9), ν_2 (position of $^{37}\text{ClONO}_2$ (4), see below), ν_7 (8), and ν_9 (7) were used. The $^{14/15}\text{N}$ isotopic shifts (0.03 cm^{-1} unc.) of $\nu_3 - \nu_6$, and ν_8 were taken from Ref. (6). The inertial defect differences of ν_2 (14), and ν_4 (0.1 times experimental uncertainty), and ν_9 (both from this work) were also used. Because it was difficult to evaluate harmonic corrections for the vibrational modes, only the isotopic shifts of $\nu_1 - \nu_4$ were harmonized using factors of 1.034, 1.022, 1.013, and 1.013, respectively, for 0, VI (cf. Ref. (28)), derived from the vibrations of NO_2 (29, 30) and ClO (51).

The isotopic shifts of ν_1 and ν_2 have not been used in the calculations because they are affected by anharmonic resonances. A Fermi resonance was observed between ν_1 and $\nu_2 + \nu_6$ (e.g. 10). For

ν_2 of $^{35}\text{ClONO}_2$ an anharmonic resonance was observed causing this fundamental to be below that of $^{37}\text{ClONO}_2$. This is only possible if the perturbing state is at higher wavenumbers for the ^{35}Cl isotopomer and lower for ^{37}Cl . It seems likely that the ν_2 inertial defect difference would become smaller for one Cl isotopomer and larger for the other. Since the observed values are very similar, it was concluded that effects of the anharmonic resonance on the ν_2 inertial defect differences are small, and these parameters may be used in the force field calculation. Using values of ν_6 (8) and $2\nu_6$ (9) it may be concluded that $3\nu_6$ (unperturbed positions of *ca.* 1295 cm^{-1} and 1287 cm^{-1} for $^{35}\text{ClONO}_2$ and $^{37}\text{ClONO}_2$ respectively) is a likely perturber.

For each piece of data at most one force constant was included in the fit, chosen in general according to the largest derivatives. Initially only the fundamentals and distortion constants were used. After adjusting the force field, isotopic shifts and finally inertial defect differences were included.

The ν_2 inertial defect differences were not particularly well reproduced. There were four force constants ($f_{\nu\gamma}$, $f_{\nu\delta}$, $f_{w\gamma}$, and $f_{w\delta}$) among the fixed ones with large derivatives with respect to this parameter. A fairly sizeable adjustment of these force constants (see Table 6) reduced the residual only by *ca.* 1/3. Possible reasons for this somewhat unsatisfactory result may be for example an additional Coriolis resonance in ν_2 with similar effects on the inertial defects for both isotopomers, or the value of force constants which have not been released in the fit.

The resulting force field is given in Table 6. As can be seen in Table 7, most of the input data has been well reproduced. The knowledge of more isotopic shifts or inertial defect differences may help to determine all of the ClONO_2 force constants. Inertial defects calculated from the force field are given in Table 8; they may be of help for the assignment of vibrational satellites in the pure rotational spectrum of ClONO_2 .

(b) Discussion

The experimental and *ab initio* force fields are quite similar; in many cases changes in the constants are smaller than 10 % (*cf.* Table 6). Because strong mixing occurs between ν_3 - ν_6 it is not surprising that the potential energy distribution (PED) and the isotopic shifts for these fundamentals differ substantially between the experimental and *ab initio* force field. The *ab initio* C/O stretching force constant is smaller than the experimental one; this is consistent with the longer C/O bond length (170.7 pm (27) versus 167.3 pm experimentally (15)). This kind of deviation is rather typical for CCSD(T)/TZ2P calculations. It should be pointed out that the agreement between experimental and calculated C/O bond length and total dipole moment was better at the MP2/TZ2P level (32).

The C/O force constant in ClONO_2 is slightly larger than the one in Cl_2O , but much smaller than in ClO (*cf.* Table 9). The trend is opposite for the C/O bond lengths, as is usually the case. Since the ionic- and π -character of the C/O bonds in ClONO_2 and Cl_2O are very similar (*cf.* Table 4), it may be concluded that the strengthening of the C/O bond in ClONO_2 is caused by a stronger σ -bond. The NO stretching force constant and bond lengths in ClONO_2 and NO_2 are essentially the same, but the NO, NO interaction force constants differ substantially.

In Ref. (15) the relationship between (a) the electronegativity of X (or better XO) and (b) the structural parameters $r(\text{ON})$, $r(\text{N}=\text{O})$, and $\angle(\text{O}=\text{N}=\text{O})$ in XONO_2 molecules has been pointed out. The ONO angle is a particularly sensitive probe, because that angle changes from 180° in NO_2^+ (34) over *ca.* 134° in the NO_2 radical (29) to about 116° in NO_2^- (25). Given the fact that the ONO angle in ClONO_2 is essentially the same as in NO_2 , it can be concluded that the electronegativities of the C/O and NO_2 groups are very similar, that the electron density at the N atom in NO_2 changes only marginally.

nally upon the formation of ClONO₂, and that the ON bond in this molecule has very little ionic character.

The P1D and the Cartesian displacement of the normal coordinates indicate that ν_1 , ν_2 , ν_8 , and ν_9 are essentially unmixed and well described as asymmetric anti symmetric NO₂ stretching, out-of-plane, and torsional mode respectively, in agreement with most other assignments (see e. g. Ref. (6)). For the remaining modes the situation is more complex. Both ν_3 and ν_4 have substantial ClO stretching and NO₂ bending character (cf. Fig. 5). They are best described as asymmetric and symmetric combinations of these modes: $\nu_3 = \{ \nu(\text{ClO}) + \delta(\text{NO}_2) \}_{\text{as}}$ and $\nu_4 = \{ \nu(\text{ClO}) + \delta(\text{NO}_2) \}_{\text{s}}$. Both ν_5 and ν_6 have substantial ON stretching character (see Table 6 and Fig. 5), but are rather difficult to describe appropriately in terms of internal coordinates. The ν_7 vibration is also somewhat complex, but it is reasonably well described as a ClON bending mode.

V. CONCLUSION

The pure rotational spectra of ClONO₂ in the ground and $\nu_9 = 1$ states have been reinvestigated. Improved and newly determined spectroscopic constants permit accurate predictions of line positions well into the submillimeter region for both ³⁵Cl and ³⁷Cl isotopomers. The complete quadrupole tensor has been determined for the first time, revealing a largely covalent ClO bond. The force field calculation indicates a slightly stronger ClO bond than in Cl₂O, consistent with the shorter bond length. In addition, it has enabled the description of the normal modes in terms of internal coordinates.

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“Table Caption

- TABLE 1** Accidental Near-Degeneracies of ClONO₂ Investigated in This Study and Energy Differences ΔE (MHz).
- TABLE 2** Observed Frequencies of Rotational Transitions (MHz) of ClONO₂, Uncertainties, and Residuals^a (O-C) (kHz).
- TABLE 3** Rotational (MHz), Centrifugal Distortion (or Differences) (kHz), Quadrupole Coupling Constants (MHz), and Inertial Defects (amu Å²) of ClONO₂, and Weighted Standard Deviation of the Fit.
- TABLE 4** Cl Quadrupole Coupling Constants and Derived Parameters of ³⁵ClONO₂, $v = 0$, in Comparison to Related Molecules.
- TABLE 5** Spectroscopic Constants^a, Standard Deviations (cm⁻¹), and Inertial Defects Δ_4 (amu Å²) of the ν_4 Band Using Ground State Constants of the Present Study.
- TABLE 6** Harmonic Force Constants (N m⁻¹) and Potential Energy Distribution (PED) of ClONO₂.
- TABLE 7** Experimental Vibrational Wavenumbers ν_i , isotopic Shifts $\Delta \nu_i^a$ (cm⁻¹), Quartic Centrifugal Distortion constants (kHz), and Inertial Defect Differences $\Delta \Delta_i^c$ (amu Å²) of ClONO₂ in Comparison to Values Calculated from the Force Field.
- TABLE 8** Inertial Defects Δ_i (amu Å²) of ClONO₂ for Various Vibrational Modes.
- TABLE 9** Comparison of Selected Force Constants (N m⁻¹) and Structural Parameters (pm, deg.) of ClONO₂ with those of Related Molecules.

Fig. 3. The $23_{7,17} - 22_{7,15}$ transition of $^{35}\text{ClONO}_2$ in the ground vibrational state. (a) Experimental spectrum, (c) simulated spectrum without χ_{ab} , (b) simulated spectrum with χ_{ab} , the shifts due to χ_{ab} are indicated by dashed lines.

Fig. 2. Detail of the energy level diagram of $^{35}\text{ClONO}_2$ in the ground vibrational state. (a) Unsplit, unperturbed level, (b) splitting caused by the Cl nucleus, (c) perturbations through χ_{ab} . Order anti quantum number assignment reversed on the left hand side.

Fig. 3. The $24_{6,18} - 22_{7,15}$ transition of $^{35}\text{ClONO}_2$ in the ground vibrational state.

Fig. 4. Principal inertial and quadrupole axes of $^{35}\text{ClONO}_2$ and one possible direction of the dipole moment. Dipole components from Ref. (4); suggested direction of the arrows is from + to -.

Fig. S. The Cartesian Displacements of the ν_3 to ν_7 normal coordinates. The vectors are lengthened for clearness.

Isotopomer	Vibrational State	Upper level	Lower level	ΔE
$^{35}\text{ClONO}_2$	ground state	$24_{6,18}$	$23_{7,16}$	42.6
		$23_{7,17}$	$24_{6,19}$	243.2
$^{37}\text{ClONO}_2$	ground state	$17_{4,13}$	$16_{5,11}$	69.0
		21_{12}	23_{11}	52.5
$^{35}\text{ClONO}_2$	$\nu_9 = 1$	$19_{6,13}$	$20_{5,15}$	226.0
$^{37}\text{ClONO}_2$	$\nu_9 = 1$	$21_{5,17}$	$20_{6,15}$	1010.8
		$21_{5,16}$	$20_{6,14}$	1755.5

(a) $^{35}\text{ClONO}_2, v = 0$

$J'_{Ka',Kc'} - J''_{Ka'',Kc''} J^{\ast b}$	Obs. Freq.	Unc.	O-C
28 _{4,25} -282,26	± 3	96304.430	35 -16
	± 1	96307.224	35 -11
54 _{8,46} -547,47	± 3	96627.551	20 -14
	± 1	96628.925	20 10
47 _{8,39} -477,40	± 1	98222.265	30 -21
	± 3	98223.219	30 -10
46 _{6,40} -466,4,	± 3	98390.959	50 53
	± 1	98394.580	50 -102
45 _{6,39} -45,40	± 3	99211.665	35 -17
	± 1	99214.638	35 -2
24 _{6,18} -245,19	+3	99270.553	15 -10
	-1		
	-3	99273.244	15 -7
	+1	99275.320	15 5
50 _{7,43} - 50 _{6,44}	± 1	99286.759	30 -4
16 _{6,10} - 16 _{5,11}	± 1	104524.078	35 5
21 _{3,19} - 20 _{3,18}	± 1	105101.293	25 1
	± 3	105101.662	2.5 29
29 _{,,,,-} - 29 _{3,26}	± 3	105345.212	25 6
	± 1	105345.776	25 -]
33 _{,,,,-28} -335,2 ₉	± 3	105422.633	25 -13
	± 1	105423.948	25 -12
28 _{3,26} - 28 _{2,27}	± 3	105438.355	35 -3
	± 1	105442.051	45 -10
55 _{9,46} -55847	± 1	105523.422	30 1
	± 3	105524.069	30 -15
44 _{,,,,-} -45,7	± 3	106157.708	40 15
	± 1	106159.142	40 17
21 _{4,18} - 20 _{4,17}		106863.779	55 -13
34 _{6,29} - 34 _{5,30}	± 3	106878.837	50 -15
	± 1	106880.263	40 -9
27 _{S₂₃} -273,24		107413.731	40 -51
34 _{7,27} -346,28	± 1	107587.345	50 5
	± 3	107588.239	50 -8
61 _{9,52} - 6 _{8,s3}	± 3	107645.236	30 3
15 _{3,13} - 14 _{2,12}	± 3	107649.167	50 59
25 _{13,} - 2612,	± 3	107742.010	50 -30
	± 1	107745.389	40 -16

$J'_{Ka',Kc'} - J''_{Ka'',Kc''}$	I'^{*b}	Obs. Freq.	Unc.	O-C
41 _{3,38} -403,37		20121 5.050	70	39
40 _{32,} -3932,	± 1	201318,158	100	155
	± 3	201320.002	100	-2
40 _{30,} -39 _{30,}	± 1	201386.922	100	40
	± 3	201388.622	100	-18
40 _{29,} -39 _{29,}	± 1	201422.699	100	-81
	± 3	201424.393	100	-28
40 _{27,} -3927,	± 1	201498.605	100	-119
	± 3	201500.110	100	-35
40 _{26,} -39 _{26,}	± 1	201539.416	100	6
	± 3	201540.810	100	84
41 _{4,38} -40 _{3,37}		201575.531	70	-37
40 _{25,} -39 _{25,}	± 1	201582.423	100	-18
	± 3	201583,762	100	105
40 _{24,} -39 _{24,}	± 1	201628.267	100	-59
	± 3	201629.475	100	29
40 _{23,} -3923,	± 1	201677.672	100	-20
	± 3	201678.799	100	81
40 _{22,} -3922	± 1	201731.332 ^d	100	21
	± 3	201732.304	100	66
40 _{21,} -3921,	± 1	201790.143	100	8
	± 3	201791.066	100	79
40 _{14,} -39,4		202513.087	70	21
40 _{11,} -39,0		203720.558	70	37
40 _{8,33} -39 _{8,32}		205025.985	70	-46
45,45-44,44		205365.292	70	5
40 _{11,} -39 _{11,}		205378.824	70	-157
43 _{37,41} -423,40		205442.491	70	-103
43 _{27,41} -422,40		205446,950	70	-30
40 _{6,34} -396,33		211585.587	70	59
73 _{24,} -7224		369080.062	45	-3
72 _{14,59} -71,4,58		369175.448	40	-17
72 _{14,58} -71,4,57		369260.559	40	-21
73 _{23,} -7223,		369322.644	40	7
73 _{8,65} -72 _{8,64}		369431.781	40	-38
61 _{20,} -61 _{19,}	± 3	369539.936	60	-48
	± 1	369540.590	80	33
73 _{22,} -72 _{22,}		369595.732	40	6
60 _{11,} -60 _{19,}	± 3	369780.098	40	-10
	± 1	369780.738	40	33

$J'_{Ka',Kc'}$	$J''_{Ka'',Kc''}$	F'^{*b}	Obs. Freq.	Unc.	O-C
59 ₂₀	-5919,	± 3	370008.770	50	-30
56 ₂₀	-5619,	± 3	370630.351	50	-9
		± 1	370631.062	50	-3
83 _{9,74}	-829,73		418615.448	60	-8
85 ₂₈	- 84 ₂₈		429261.222	80	-54
95 ₅	-94,94		430102.879	70	-102
94 ₉₃	- 93 ₉₂		430109.012	70	-13
82 _{13,69}	-8 1 _{13,68}		430116.881	80	-76
93 ₉₁	-92,90		430119.920	70	47
92 ₈₉	-91 ₈₈		430142.166	70	79
85 ₂₄	-84 ₂₄		430422.487	70	48
84 _{16,68}	- 83 _{16,67}		430821.049	60	-27
86 _{17,70}	-85 _{17,69}		440148.795	60	6
86 _{7,69}	- 85 _{17,68}		440164.217	60	7
87 ₂₅	- 86 ₂₅		440315.102	60	26
88 _{10,79}	- 87 _{10,78}		440418.932	60	33
88 _{9,79}	-87 _{9,8}		440502.091	60	40

(b) $^{37}\text{ClONO}_2$, $v = 0$

$J'_{Ka',Kc'}$	$J''_{Ka'',Kc''}$	F'^{*b}	obs. Freq.	Unc.	O-C
17 _{5,12}	- 16 _{5,11}	+1	84165.265	20	-2
		- 3	84165.632	20	-15
		- 1	84166.467	15	-11
		+3	84167.233	15	5
17 _{4,13}	- 16 _{4,12}	- 1	84872.681	20	18
		+3			
		- 3	84873.936	20	-21
		+1	84874.241	20	27
18 _{4,14}	-17 _{4,13}	+1	90126.423	20	-16
		- 3	90126.746	20	30
		-1	90127.98	20	4
		+3			
19 _{2,18}	- 18 _{2,17}	± 1	90230.320	25	-3
		± 3	90230.622	25	25
20 ₂₀	- 19 _{1,19}		90423.363	25	-5
20 ₂₀	-19 _{1,19}		90495.903	20	-21
20 _{0,20}	- 19 _{0,19}		90528.660	25	-7

$J'_{Ka',Kc'} - J''_{Ka'',Kc''}$	J'^{*b}	Obs. Freq.	Unc.	O-C
$19_{1,18} - 18_{1,17}$	± 1	91049.799	20	-1
	± 3	91050.243	20	3
$18_{2,16} - 17_{2,15}$	± 1	91473.761	20	-17
	± 3	91474.135	20	0
$19g, -189,$	± 1	93568.222	30	22
	± 3	93569.364	30	21
$198,-188,$	± 1	93644.146	35	-8
	± 3	93645.034	35	-11
$49_{8^{+41}}-497,42$	± 1	96972.939	25	-10
	± 3	96973.585	25	-8
$31_{5,27}-31_{4,28}$	± 3	9722.0.122	40	-14
	± 1	97221.751	40	-52
$51_{7,44}-516,45$	± 3	97440.595	40	-21
$20_{17,-} - 19_{17,-}$	$+1$	98261.777	30	-34
	-1	98262.136	25	-17
	$+3$	98265.338	25	-38
	-3	98265.730	20	12
$38_{7,31} - 38_{6,32}$	± 3	98628.840	50	2
$41_{5,36} - 414,3,'$	± 3	98642.125	35	-8
	± 1	98644.810	35	-10
$56_{8,48} - 56_{7,49}$	± 3	98860.013	40	-16
	± 1	98861.190	40	-6
$20_{3^{+17}} - 19_{3,16}$		102713.605	30	0
$37_{4,33} - 37_{3,34}$	± 3	104509.035	40	-12
	± 1	104511.908	35	-14
$47_{6,41}-475,42$	± 3	104517.012	30	-19
	± 1	104519.417	30	16
$26_{3,23} - 25_{4,22}$	± 3	104834.320	35	-14
	± 1	104836.068	35	13
$22_{2,2}, - 21_{1,20}$	± 1	105059.552	25	3
	± 3	105060.060	25	-8
$29_{2,27}- 29_{1,28}$	± 3	105299.222	35	12
	± 1	105302.335	35	34
$16_{6,10} - 16_{5,11}$	-3	105314.250	50	40
	$+3$	105316.066	50	5
	$+1$			
$30_{4^{+26}} - 29_{5,25}$	± 3	106260.408	30	16
$33_{3,30} - 33_{2,31}$	± 3	106778.398	60	-54
	± 1	106781.386	60	8
$32_{4^{+25}}-323,30$	± 3	107544.037	50	61

$J'_{Ka',Kc'}$	$J''_{Ka'',Kc''}$	I'^{*b}	Obs. Freq.	Unc.	O-C
32_{4,29}-323,30		± 1	107546.432	50	38
356,30-355,31		± 3	107608.557	40	-5
		± 1	107609.648	40	-11
2213, -21₁₃,		± 1	108208.872	40	0
		± 3	108210.440	40	15
2212,- 21₁₂,		+1	108247.743	20	-14
		-1	108248.093	20	-8
		+3	108249.071	20	-15
		-3	108249.417	20	-4
64_{10,54} - 64_{9,55}		± 1	115760.196	25	-5
		± 3	115760.668	25	14
39_{6,34} - 39_{5,35}		± 3	116208.906	2s	17
		± 1	116210.314	25	17
54_{7,47}-546,48		± 3	116658.845	25	17
31_{7,24}- 3_{16,25}			116903.404	30	10
26_{1,26}- 25_{1,25}			116976.489	20	-2
25_{2,24} - 24_{2,23}			116978.451	35	0
26_{1,26}-251,25			116983.675	25	-7
26_{1,26} - 25_{0,25}			116987.131	25	-11
26_{1,26} - 25_{0,25}			116994.329	20	-5
25_{1,24} -241,23		± 1	117130.595	20	-10
		± 3	117130.847	20	14
23_{4,19} - 22_{4,18}			117214.065	30	-7
353_{3,32}-352,33		± 3	117394.198	40	0
		± 1	117396.808	30	-50
24_{2,22} -2.322		+1	117856.702	20	-19
		-1	117857.031	20	28
		+3	117860.160	20	-15
		-3	117860.475	20	17
24_{1,19} -23,9,		± 3	117912.643	40	-15
24_{1,18} -23,8,		± 1	117930.680	40	-10
		± 3	117932.982	40	-12
24_{1,17} - 23_{1,17},		± 1	117953.454	30	-3
23_{3,20}- 22_{3,19}			117954.790	40	s
24_{1,17}-2316,		± 1	117979.034	30	-13
		± 3	117980.854	30	-10
24_{1,15} -23,5,		± 1	118008.334	30	-14
		± 3	118009.932	30	-11
24_{1,14} - 23_{1,14},		± 1	118042.586	30	5
		± 3	118043.981	30	14

$J'_{Ka',Kc'} - J''_{Ka'',Kc''}$	J'^{*b}	Obs. Freq.	Unc.	O-C
$24_{13} - 23_{13}$	± 1	118083.466	30	-12
	± 3	118084.665	30	-7
$24_{12} - 23_{12}$	± 1	118133.459	30	-10
	± 3	118134.474	30	-6
$39_{18} - 38_8$	± 1	191926.633'	100	91
$41_{2,39} - 40_{3,38}$		192011.149	70	-164
$41_{3,39} - 40_{3,38}$		192042.804	70	0
$41_{2,39} - 40_{2,38}$		192056.138	70	-32
$41_{3,39} - 40_{2,38}$		192087.809	70	148
$39_{8,31} - 38_{3,30}$		194726.884	70	-3
$40_{2,19} - 39_{21}$		196671.760	70	251
$40_{99} - 39_{19}$		196797.423	70	-8
$40_{8,} - 39_{8,}$		196872.912	70	54
$40_{7,} - 39_{7,}$		196959.581	70	33
$40_{15,} - 39_{5,}$		197180.511	70	81
$40_{2,2} - 39_{2,}$		197726.070	70	-25
$40_{4,36} - 39_{4,35}$		198264.377	70	60
$40_{0,3} - 39_{0,30}$		198401.659	70	-212
$40_{10,30} - 39_{10,29}$		198404.239	70	-149
$41_{28,} - 40_{28,}$	± 1	201283.561	100	-82
	± 3	201284.780	100	20
$41_{27,} - 40_{27,}$	± 1	201321.528	100	28
	± 3	201322.539	100	1
$41_{2,} - 40_{25,}$	± 1	201403.247	100	85
	± 3	201403.994	100	-56
$41_{23,} - 40_{23,}$		201496.311	70	14
$41_{15,4} - 40_{15,4}$		202150.711	70	61
$42_{23,} - 41_{23,}$	± 1	206424.542	100	104
	± 3	206425.238	100	104
$42_{22,} - 41_{22,}$		206480.337	70	212
$42_{20,} - 41_{20,}$		206608.388	70	-4
$42_{4,38} - 41_{3,7}$		206610.926	70	66
$42_{18,4118,}$		206770.345	70	-63
$51_{50} - 50_{49}$		231622.019	70	-31
$75_{27,} - 74_{27,}$		368967.112	60	-9
$75_{26,} - 74_{26,}$		369141.796	4s	-19
$74_{10,65} - 73_{10,64}$		369187.038	40	-32
$75_{9,67} - 74_{9,66}$		369270.885	70	-64
$75_{25,} - 74_{25,}$		369333.562	50	-45
$73_{9,64} - 72_{9,63}$		369477.727	50	-24

$J'_{Ka',Kc'} - J''_{Ka'',Kc''} F^{*b}$	Obs. Freq.	Uric.	o-c
$75_{24}, -74_{24},$	369545.778	45	-16
$75_{23}, -74_{23},$	369782.480	40	-1
$75_{22}, -74_{22},$	370048.847	45	-10
$75_{19}, -74_{19},$	371103.723	45	22
$97_{97}, -96_{97},$	429241.636	80	-40
$96_{99}, -95_{94},$	429247.704	80	27
$95_{93}, -94_{92},$	429258.463	120	-16
$94_{99}, -93_{90},$	429280.656	70	35
$89_{9,81}, -88_{9,80},$	430123.554	100	-33
$89_{11,79}, -88_{11,78},$	440029.444	70	62
$88_{,,,,}, -87_{12,76},$	440053.188	70	-5
$88_{16,72}, -87_{(),7},$	440074.513	70	20
$87_{14,73}, -86_{14,72},$	440552.979	60	9
$89_{21}, -88_{21},$	440622.492	60	26
$86_{13,73}, -85_{13,72},$	440708.404	60	-1

(c) $^{35}\text{ClONO}_2, \nu_9 = 1$

$J'_{Ka',Kc'} - J''_{Ka'',Kc''} F^{*b}$	Obs. Freq.	Unc.	O-C
$30_{6,24}, -30_{5,25}, \pm 1$	84377.579	25	-15
$27_{2,25}, -27_{1,26}, \pm 3$	97881.552	50	-5
± 1	97885.616	50	-3
$31_{5,27}, -31_{4,28}, \pm 3$	97964.118	40	-14
± 1	97966.311	40	4
$50_{7,43}, -50_{6,44}, \pm 3$	98620.904	40	-26
± 1	98623.204	40	-19
$31_{3,28}, -31_{2,29}, \pm 3$	99231.503	40	-5
± 1	99235.322	40	-11
$51_{7,44}, -51_{6,45}, \pm 3$	104874.346	35	-2
± 1	104876.845	35	10
$56_{8,48}, -56_{7,49}, \pm 3$	104906.856	50	-6
± 1	104908.771	35	-7
$41_{5,36}, -41_{4,37}, \pm 3$	105200.435	30	-1
± 1	105203.731	30	13
$20_{3,17}, -19_{3,16},$	105555.116	50	-6
$21_{11}, -20_{11}, \pm 1$	106121.470	35	14
± 3	106123.065	35	10
$23_{1,23}, -22_{1,22},$	106281.347	30	-4

$J'_{Ka',Kc'}$	$J''_{Ka'',Kc''}$	I'^{*b}	Obs. Freq.	Unc.	O-C
23 _{0,23}	220,22		106289.769	30	-29
61 _{9,52}	61 _{8,53}	± 3	106806.667	25	-3
		± 1	106807.942	25	-6
21 _{5,16}	20 _{5,15}	-1	107468.323	25	-37
		+3	107468.841	25	-2
		+1	107469.012	18	-18
		-3	107469.303	18	13
21 _{2,19}	20 _{2,18}	± 1	107662.094	25	-4
		± 3	107662.701	20	-2
21 _{4,17}	20 _{4,16}		109395.555	30	7
42 _{8,34}	42 _{7,35}	± 1	115823.258	30	-1
		± 3	115824.363	30	13
63 _{9,54}	63 _{8,5}	± 1	116646.489	30	-7
61 _{10,51}	61 _{9,52}	± 1	117180.785	30	-11
		± 3	117181.575	30	-17
58 _{8,50}	58 _{7,51}	± 3	117519.176	30	-3
		± 1	117521.509	30	13
31 _{7,25}	31 _{6,26}	± 3	117851.588	30	8
		-1	117852.150	30	2
38 ₃₀	3730,	± 1	191447.632	100	-164
		± 3	191449.786	100	-39
38 ₂₉	3729,	± 1	191479.957	100	-195
		± 3	191482.079'	100	47
38 ₂₈	3728,	± 1	191513.488	100	-57
		± 3	191515.381	100	69
38 ₂₇	3727,	± 1	191548.219	100	-6
		± 3	191549.972	100	106
38 ₂₆	3726,	± 1	191584.504	100	17
		± 3	191586.215	100	207
38 ₂₅	3725,	± 1	191622.721	100	32
		± 3	191624.284	100	190
38 ₂₃	3723,	± 1	191706.702	100	-45
		± 3	191707.913	100	-21
38 ₂₂	3722,	± 1	191753.718	100	-77
		± 3	191754.919	100	43
38 ₂₁	3721,		191835.470	70	45
38 ₁₉	3719,	± 1	191925.634	100	-13
		± 3	191926.633'	100	91
38 ₁₇	3717,		192080.475	70	-109
38 ₁₄	3714,		192427.972	70	-19

$J'_{Ka',Kc'} - J''_{Ka'',Kc''}$	F'^{*b}	Obs.Freq.	Uric.	O-C
37 _{5,32} - 365,3,		195229.815	7 0	-138
40 _{4,37} - 394,3,		196731.873	70	-104
39 _{21,} - 38 _{21,}		196870.700	7 0	-119
38 _{7,31} - 377.30		196985.741	70	63
39 _{13,} - 3813,		197722.490	70	73
394,3s - 384,34		198347.607	70	-47
444, - 43, 43		2.01184.472	70	-70
41 _{4,38} - 404,37		201249.514	70	-17
41 _{,,38} - 403,37		201385.571	70	-28
40 _{25,} - 39 _{25,}	± 3	201731.332 ^d	100	21
40,* - 39,8,		202157.755	70	-48
73 _{25,} - 72 _{25,}		369115.977	45	13
71 _{12,59} - 70,,,,,		369138.499	45	-13
73 _{4,9} - 72,4,		369332.294	40	23
34 _{11,} - 33,,	± 3	369514.057	60	-7
	± 1	369514.814	60	71
73 _{23,} - 7223,		369573.668	so	29
1915, - 18 _{14,}	± 3	370654.927	50	28
	± 1	370656.046	50	-28
83 _{32,} - 82 _{32,}		418618.306	7 0	-103
81 _{13,69} - 80 _{13,68}		418652.912	60	15
92 _{,,9} - 9] ,88		430703.944	60	-49
85,,, - 8424,,		430706.262	120	190
93 ₉₁ - 92 ₉₀		430732.553	50	-34
94 ₉₃ - 93 ₉₂		430772.618	60	18
95 ₉₅ - 94,9,,		430817.633	60	67
89 _{9,81} - 88 _{9,80}		440193.765	60	-15
89 _{8,81} - 88 _{8,80}		440199.674	60	-25
87 _{26,} - 8626		440283.309	60	4
86 _{7,70} - 85 _{17,69}		440414.256	60	-2
86 _{17,69} - 85 _{17,68}		440430.183	60	6
87 _{25,} - 8625,		440605.313	60	4

((t) ³⁷C10N0₂, $\nu_9 = 1$

$J'_{Ka',Kc'} - J''_{Ka'',Kc''}$	F'^{*b}	Obs. Freq.	Unc.	O-C
51 _{7,44} - 51 _{6,45}	± 3	96770.514	30	12
4 _{6,40} - 4 _{6,4,4}	± 1	97253.602	25	-9

$J'_{Ka',Kc'} - J''_{Ka'',Kc''} I'^{*b}$	Obs. Freq.	Uric.	O-C
$41_{5,36} - 41_{4,37} \pm 3$	97952.649	30	-10
$20_{13,} - 19_{13,} \pm 1$	98416.947	30	8
± 3	98419.00S	30	-9
$20_{12,} - 19_{2,} \pm 1$	98446.942	25	15
± 3	98448.683	25	-10
$20_{11,} - 19_{11,} \pm 1$	98484.154	25	-1
± 3	98485.616	25	-19
$20_{,} - 19_{,} \pm 1$	98595.248	25	-5
± 3	98596.215	25	-16
$30_{4,27} - 30_{3,28} \pm 3$	98662.025	30	8
± 1	98664.418	30	14
$20_{8,} - 19_{8,} \pm 1$	98683.222	25	-1
± 3	98683.976	25	-7
$48_{8,40} - 48_{7,41} \pm 1$	98769.268	25	-4
± 3	98770.046	25	1
$32_{5,28} - 32_{4,29} \pm 3$	98873.756	25	2
± 1	98875.466	25	-1
$20_{6,15} - 19_{6,14} \pm 1$	99008.840	30	-4
± 3	99009.247	25	16
$20_{6,14} - 19_{6,13} \pm 1$	99020.394	30	-9
± 3	99020.799	25	12
$21_{2,20} - 20_{2,19}$	99301.328	50	-7
$20_{5,15} - 19_{5,14}$	99466.705	40	-23
$22_{,}, - 21_{,}, 2,$	99478.092	25	-7
$22_{,22} - 21_{0,21}$	99493.514	30	-22
$24_{6,18} - 24_{5,19}$	99691.282	30	6
$21_{1,20} - 20_{,}, 19 \pm 1$	99788.500	25	-8
± 3	99788.864	25	12
$22_{5,18} - 21_{5,17} \pm 1$	109371.051	30	-37
± 3			
$22_{2,20} - 21_{2,19} \pm 1$	109657.386	35	-4
± 3	109657.836	35	-22
$22_{5,17} - 21_{5,16} \pm 1$	109794.476	25	-2.
± 3			
$37_{<,32} - 37_{5,33} \pm 3$	110243.544	40	-3
± 1	110244.784	40	-5
$39_{21,} - 38_{21,}$	191880.655	70	-237
$39_{20,} - 38_{20,}$	191936.111	70	-155
$39_{18,} - 38_{8,}$	192068.289	70	55
$39_{,77} - 38_{17,}$	192148.722	70	79

$J'_{Ka',Kc'} - J''_{Ka'',Kc''}$	F'^{*b}	Obs. Freq.	Unc.	O-C
$40_{4,37} - 39436$		192320.197	7 0	-123
$39_{15,3} - 815,$		192353.280	70	215
$38_{5,33} - 37_{5,32}$		195257.891	70	-92
$40_{18,} - 3918,$		197017.709	70	192
$40_{0,3} - 39_{0,30}$		198538.919	70	92
$412_{1,} - 4021,$		201754.404	70	-209
$41_{19,} - 4019,$		201888.378	70	3
$41_{18,} - 4018,$		201968.504	7 0	-167
$4115, - 40_{15,}$		202297.043	70	42
$4112, - 4012,$		202881.897	70	27
$41_{8,34} - 40_{,,,}$		204872.,545	70	23
$76_{7,69} - 75_{7,68}$		369074.337	45	-45
$72_{11,6} - 71_{11,60}$		369139.605	60	2
$75_{27,} - 74_{27,}$		369226.962	45	37
$75_{9,67} - 74_{9,66}$		369471.776	50	0
$73_{9,64} - 72_{9,63}$		369533.371	50	0
$75_{25,} - 7425$		369591.606	60	6
$7s_{24,} - 7424$		369802.734	40	3
$75_{23,} - 74_{23}$		370038.238	45	-1
$23_{14,} - 22,3,$	± 3	370614.267	50	20
	± 1	370615.250	60	-29
$88_{16,73} - 87_{16,72}$		440229.769	100	-25
$88_{12,77} - 87_{12,76}$		440236.798	80	51
$89_{11,79} - 88_{11,78}$		440239.132	80	35
$88_{16,72} - 87_{16,71}$		440342.710	60	-29
$89_{22,} - 88_{22,}$		440396.419	70	-8

^a Observed frequency minus that calculated from the spectroscopic constants. Intensity-weighted average for blended lines.

^b $F^* - 2(F - J)$; in general for both upper and lower states, for the $\Delta J = 2$ transition both values are given. ^{c, d, e} Blended.

parameter	ground state		$\nu_9 = 1$	
	$^{35}\text{ClONO}_2$	$^{37}\text{ClONO}_2$	$^{35}\text{ClONO}_2$	$^{37}\text{ClONO}_2$
A	12105.784456 (768)	12105.326584 (1641)	12004.639909 (1438)	12003.626031 (2016)
B	2777.0009842 (1235)	2700.9741107 (1 126)	2776.8148366 (1824)	2700.8682752 (1822)
c	2258.1510524 (1286)	2207.6044577 (1 189)	2262.1330537 (1810)	2211.4684238 (1714)
D_J	0.5007004 (411)	0.4809592 (451)	0.5084924 (588)	0.4883448 (555)
D_{JK}	3.855784 (400)	3.715916 (638)	3.847448 (535)	3.708612 (873)
D_K	9.47049 (630)	9.66338 (2181)	8.09573 (596)	8.23273 (755)
$d_1 \times 10^2$	-9.579130 (1906)	-8.973687 (2153)	-9.591268 (2018)	-8.979438 (4066)
$d_2 \times 10^2$	-1.771828 (786)	-1.616437 (878)	-1.688908 (895)	-1.541817 (2049)
$(A) H_J \times 10^{10}$	-1.3772 (339)	0.1007 (440) ^a	0.0223 (489) ^a	^d
$(A) H_{JK} \times 10^7$	-5.8710 (455)	0.3934 (662) ^b	0.2203 (650) ^c	^d
$(A) H_{KJ} \times 10^8$	-1.2156 (605)	-0.2837 (1250) ^b	0.2078 (855) ^c	^d
$H_K \times 10^8$	2.683 (1059) ^a			
$h_1 \times 10^{11}$	-1.5427 (1714) ^a			
$h_2 \times 10^{12}$	-4.601 (777) ^c			
$h_3 \times 10^{12}$	3.709 (450) ^a			
χ_{aa}	-83.880 (94)	-65.968 (164)	-82.980 (191)	-66.1 I (42)
χ_-	-44.342 (21 6)	-34.6 I1 (207)	-42.859 (241)	-33.88 (32)
$ \chi_{ab} $	74.191 (87)	58.501 (154)	73.18 (72)	64.2 (48)
A_i	0.067889 (19)	0.068044 (19)	-0.690003 (29)	-0.692991 (28)
<i>rms</i>	1.106			

^aNumbers in parentheses are one standard deviation in units of the least significant figures. Watson's S-reduction in the representation Γ was used. See also text for details. ^b $4^{3,7} := H(^{37}\text{ClONO}_2) - H(^{35}\text{ClONO}_2)$.

^c $\Delta^v := H(v_9 = 1) - H(v = 0)$. ^d Both b and c applied, uncertainties propagated.

^eCommon constant for both isotopomers and both vibrational states.

parameter	ground state		$v_9 = 1$	
	$^{35}\text{ClONO}_2$	$^{37}\text{ClONO}_2$	$^{35}\text{ClONO}_2$	$^{37}\text{ClONO}_2$
<i>A</i>	12105.784223 (768)	12105.326297 (1641)	12004.639641 (1439)	12003.625722 (2016)
<i>B</i>	2777.0062903 (1234)	2700.9792387 (1 125)	2776.8198740 (1823)	2700.8731414 (1812)
<i>C</i>	2258.1458787 (1285)	2207.5994585 (1 180)	2262.1281358 (1808)	2211.4636682 (1707)
Δ_J	0.5361365 (433)	0.5132879 (499)	0.5422626 (644)	0.5191728 (754)
A_{JK}	3.643080 (436)	3.521888 (640)	3.644725 (581)	3.523543 (988)
Δ_K	9.64759 (629)	9.82422 (2175)	8.26443 (596)	8.38666 (757)
$\delta_J \times 10^2$	9.578935 (1901)	8.973836 (2137)	9.591217 (2013)	8.979647 (4067)
δ_K	2.61989 (120)	2.52976 (135)	2.49004 (135)	2.40545 (339)
(<i>A</i>) $\Phi_J \times 10^{10}$	-1.4687 (346)	0.1043 (439) ^a	0.0145 (488) ^c	^d
(<i>A</i>) $\Phi_{JK} \times 10^9$	-3.608 I (2743)	0.2643 (682) ^a	0.1726 (648) ^a	^d
(<i>A</i>) $\Phi_{KJ} \times 10^8$	-1.9694 (1076)	-0.2462 (1249) ^b	0.2206 (856) ^a	^d
$\Phi_K \times 10^8$	3.187 (1057) ^a			
$\phi_J \times 10^{10}$	-1.1664 (1654) ^a			
$\phi_{JK} \times 10^9$	-1.6235 (1 150) ^c			
$\phi_K \times 10^8$	3.372 (683) ^a			
χ_{aa}	-83.883 (94)	-65.967 (164)	-82.980 (191)	-66.11 (42)
χ_-	-44.351 (216)	-34.614 (207)	-42.870 (241)	-33.89 (32)
χ_{ab}	74.192 (87)	58.502 (154)	73.10 (72)	64.3 (48)
Δ_i	0.068749 (19)	0.068917 (19)	-0.689188 (29)	-0.692164 (28)
rms	1.107			

^a Numbers in parentheses are one standard deviation in units of the least significant figures. Watson's A-reduction in the representation Γ was used. See also part a) for further footnotes and text for details.

parameter	$^{35}\text{ClONO}_2^{\text{a}}$	$^{35}\text{Cl}_2\text{O}$	$^{35}\text{ClH}^{\text{b}}$
$\chi_{\text{aa}} / \text{MHz}$	-83.880 (94)	-71.45''	-145.8718
$\chi_{\text{bb}} / \text{MHz}$	19.769 (102)	6.86'	
$\chi_{\text{cc}} \equiv \chi_{\text{y}} / \text{MHz}$	64.111 (131)	64.59'	
$ \chi_{\text{ab}} / \text{MHz}$	74.191 (87)	- 82. ^d	
$\chi_{\text{z}} / \text{MHz}$	-122.692 (21 9)	-123.2	-145.8718
$\chi_{\text{x}} / \text{MHz}$	58.581 (337)	58.6	
η_{z}	0,0451 (29)	0.05	
$\theta_{\text{za}} \text{ I deg}$	27.532 (34)'	32.2 ^d	
$\theta_{\text{ra}} / \text{deg}$	30.28	34.6 ^d	
i_{c}	0.048	-0.048	0.29
π_{c}	0.033	-0.035	

^a This work. ^b Ref. (20). ^c Ref. (21). ^d Ref. (22); see also text.

parameter	³⁵ C10NO ₂	³⁷ C10NO ₂
ν_0	780.2163222 (371)	778.8696325 (499)
AA x103	0.131613(2417)	0.070302 (5 139)
$\Delta B \times 10^3$	-0.108609 (628)	-0.126392 (1 039)
$\Delta C \times 10^3$	-0.188068 (485)	-0.189952 (780)
Δ_4	0,4289 (23)	0.4054 (41)
rms x 10 ³	0.447	0.390

^aLine positions from Ref. (13), uncertainties 0.0005 cm⁻¹; numbers in parentheses are one standard deviation in units of the least significant figures; centrifugal distortion constants fixed to ground state values.

[illegible]

^a R = $\angle(\text{C1O})$, S = $r(\text{ON})$, v = $r(\text{NO}_e)$, w = $r(\text{NO}_i)$, $\alpha = \angle(\text{ClON})$, $\gamma = \angle(\text{ONO}_e)$, $\delta = \angle(\text{ONO}_i)$,
 oop = out-of-plane, τ = torsion. ^bFor $^{35}\text{ClONO}_2$; only contributions ≥ 0.03 arc given.

^cThis work.

^dRef. (27).

^eFixed.

^fAdjusted, see text.

para- meter	³⁵ ClO ¹⁴ NO ₂		³⁷ ClO ¹⁴ NO ₂		³⁵ ClO ¹⁵ NO ₂	
	ohs.	talc.	obs.	talc.	ohs.	talc.
(A) ν_1	1736.9	1728.4		0.01	42.8 ^d	40.03
(A) ν_2	1293.2	1291.8	-0.37 ^d	0.01	12.0 ^d	13.51
(A) ν_3	809.4	810.8	1.7	1.69	4.7	4.43
(A) ν_4	780.2	780.6	1.36	1.36	7.2	6.21
(A) ν_5	563.1	561.3	1.7	1.74	3.2	1.57
(A) ν_6	435.4	432.6	2.6	2.72	1.9	1.68
(A) ν_7	262.1	257.6		2.69		0.56
(A) ν_8	711.0	710.6		0.01	17.1	18.16
(A) ν_9	120.2	120.3		0.43		0.06
Δ_J	0.5361	0.5362	0.5133	0.5131		0.5329
A_{JK}	3.643	3.660	3.5222	3.539		3.644
AK	9.648	9.369	9.824	9.524		9.401
δ_J	0.09579	0.09575	0.08974	0.08967		0.09471
δ_K	2.620	2.567	2.530	2.478		2.552
$\Delta\Delta\nu_2$	0.1031	0.0804	0.1039	0.0804		
AA ν_4	0.3602	0.3602	0.3365	0.3360		
$\Delta\Delta\nu_o$	-0.75794	-0.75793	-0.76108	-0.76106		

^a $\Delta\nu_i^{37} := \nu_i(^{35}\text{ClONO}_2) - \nu_i(^{37}\text{ClONO}_2)$; $\Delta\nu_i^{15} := \nu_i(^{35}\text{ClO}^{14}\text{NO}_2) - \nu_i(^{35}\text{ClO}^{15}\text{NO}_2)$.

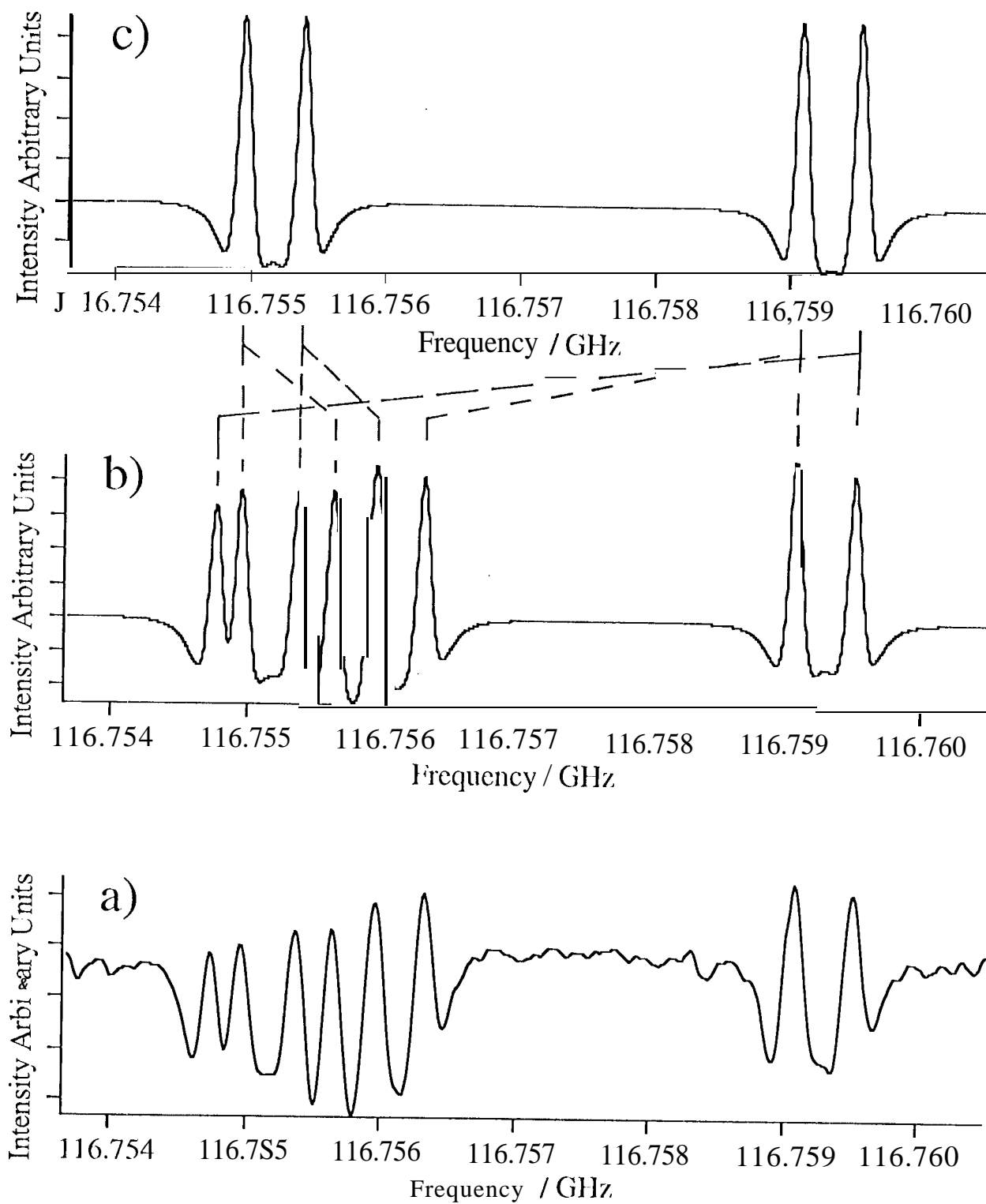
^b Watson's A-reduction, see text. ^c $A_i := A_i - \Delta_0$. ^d Not used in the fit, see text.

	³⁵ ClONO ₂	³⁷ ClONO ₂
A_{Cent}	0.000878	0.000886
Δ_0	0.065543	0.065670
Δ_1	0.036730	0.036858
Δ_2	0.145900	0.146024
Δ_3	0.142078	0.167489
Δ_4	0.425690	0.401680
Δ_5	0.330229	0.338492
Δ_6	0.261630	0.260449
Δ_7	0.566828	0.565564
Δ_8	-0.495722	-0.498789
Δ_9	-0.692384	-0.695391

	ClONO ₂	Cl ₂ O ^b	ClO	NO ₂ ^c
f_{ClO}	350.2 ^a	294.9	471.3 ^f	
$r(\text{ClO})$	167.3	169.59	156.96 ^g	
$f_{\text{N=O}}$	1088.8 ^a 1071.7 ^a			1090.6
$f_{\text{N=O,N=O}}$	117.8 ^a			193.5
$r(\text{NO})$	119.6			119.46
$\angle(\text{O=N=O})$	132.6			133.83

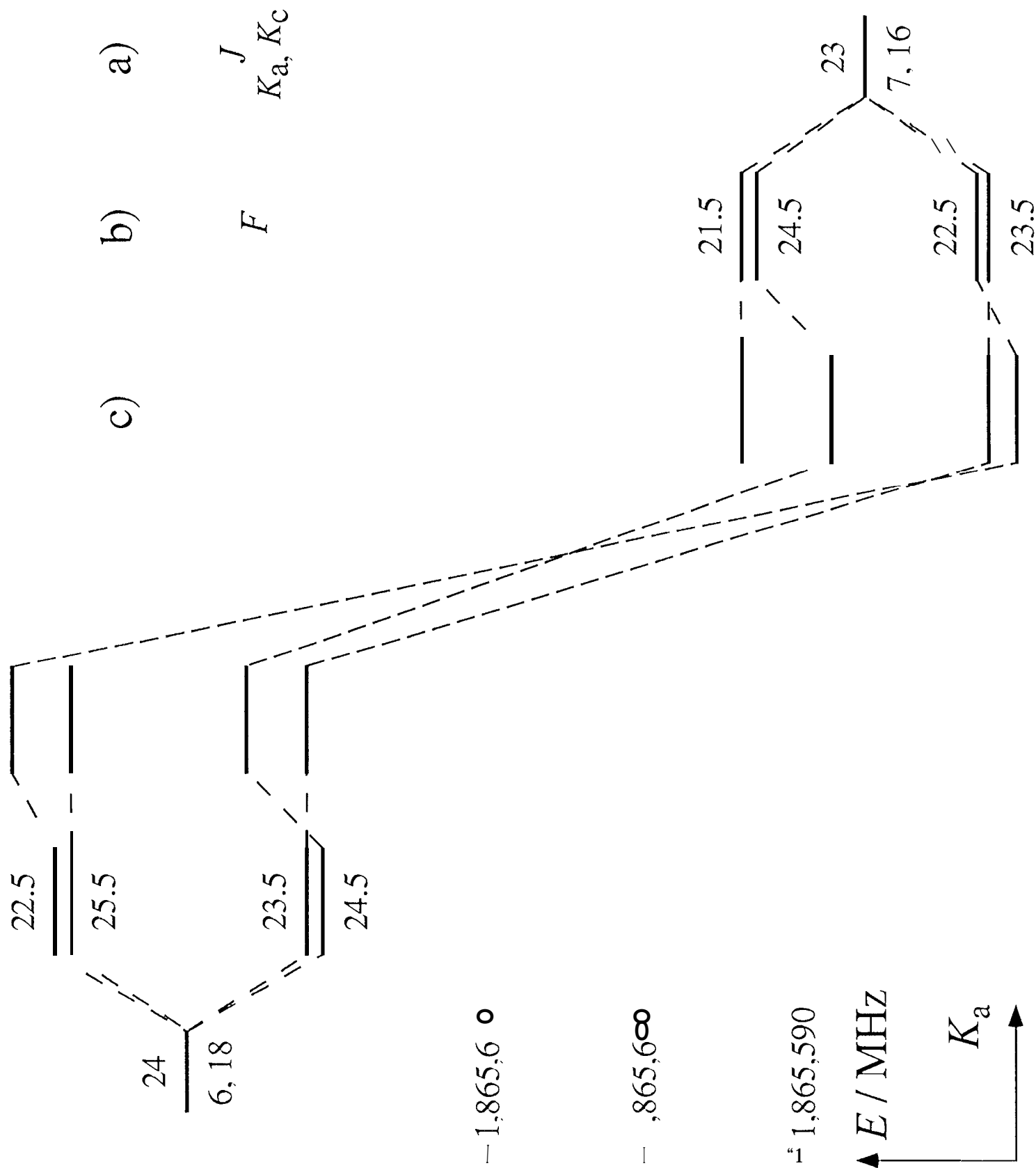
^a For ClONO₂ r_a parameters (15), r_e else. ^c Ref. (22). ^d Ref. (29).

^e This work. ^f Derived from Ref. (31). ^g Ref. (??),

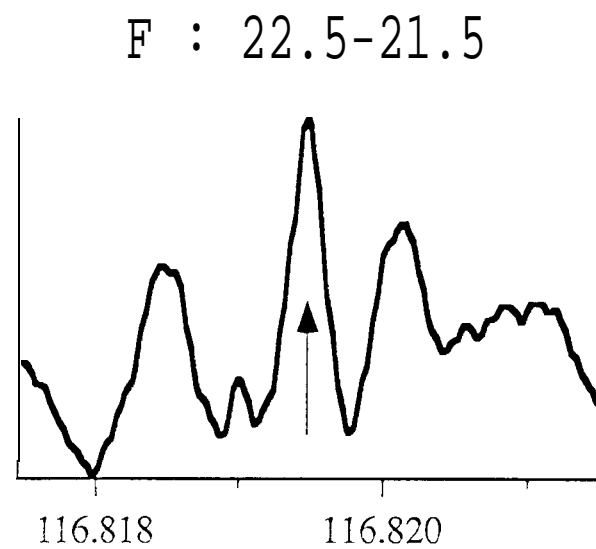
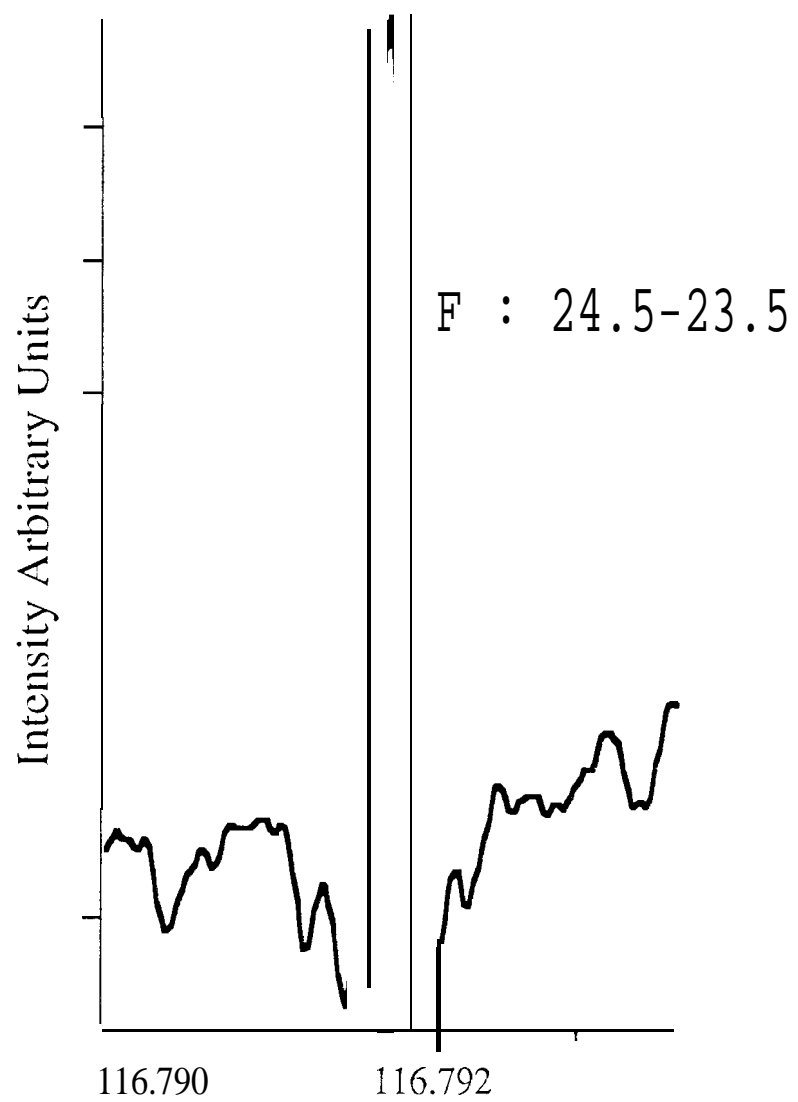


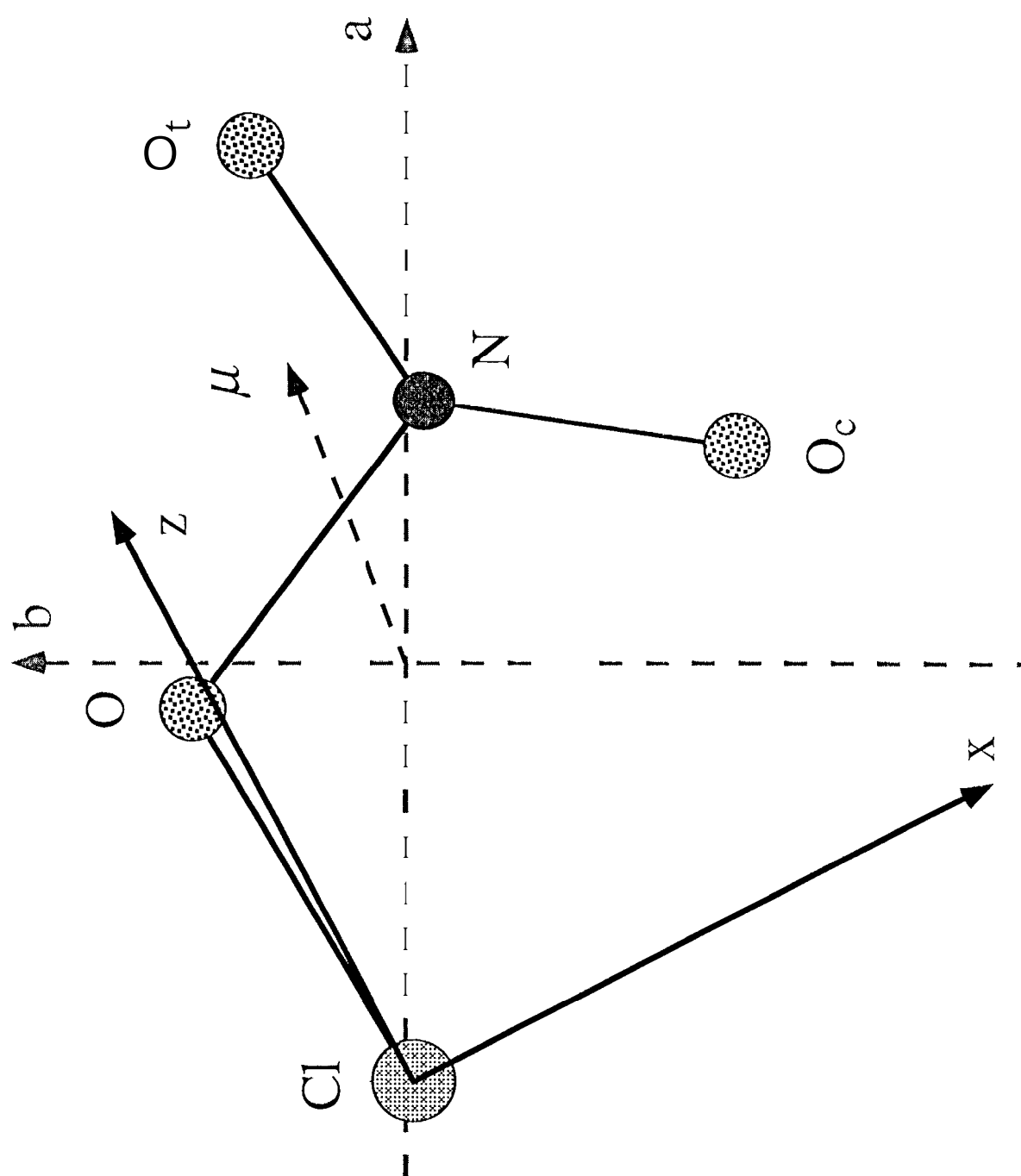
J. Pol. Sci., Kulkarni et al., Fig. 1

J. Mol. Spec., Tully et al., Fig. 2



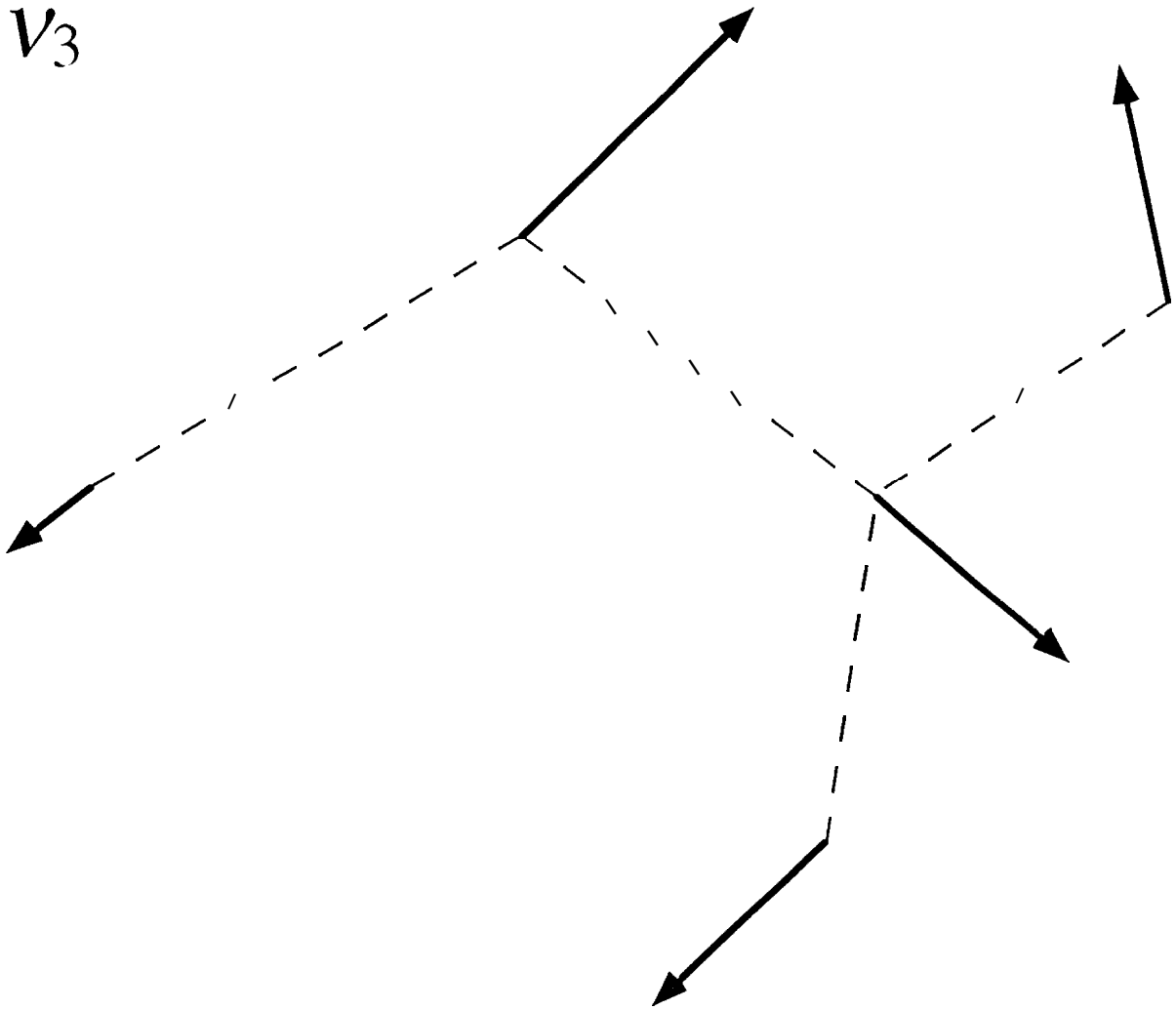
2.730 Spec. Fig 3; 9/16/88 ad.





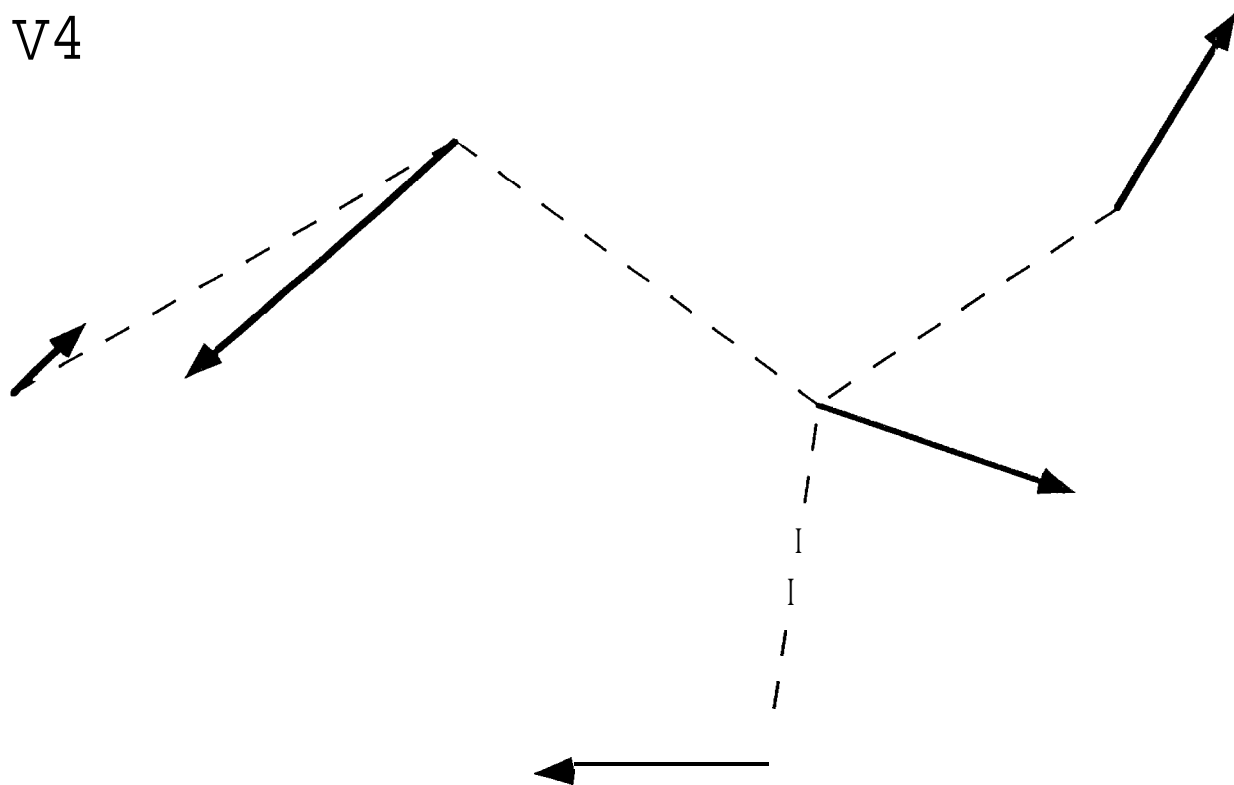
J. Mol. Spec.; Rüttli et al.; Fig. 4

V_3



Col. Spec.; Nalle et al.; Fig 5

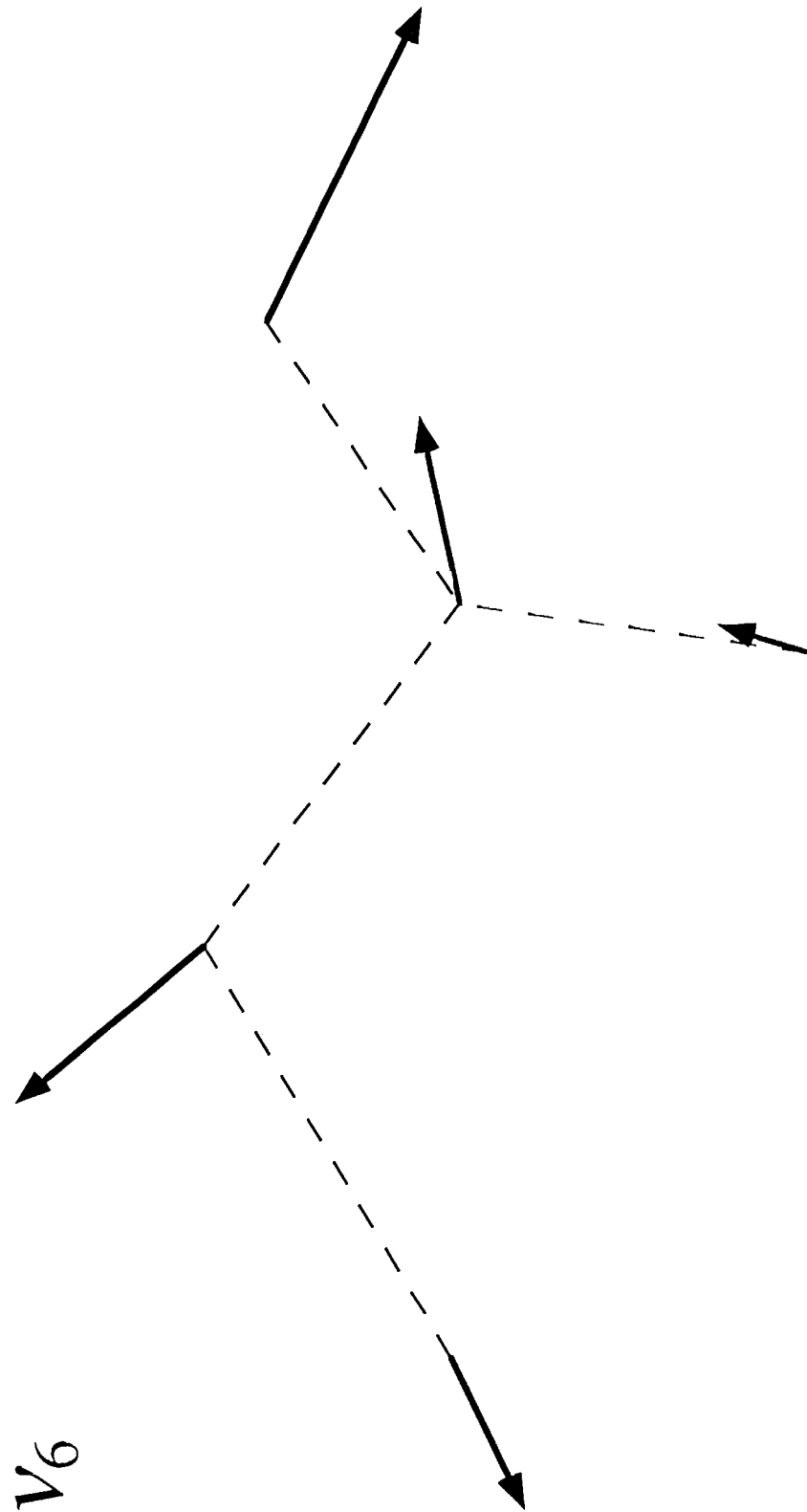
V4



J. Nat. Spec.; Kuller et al.; Fig 5



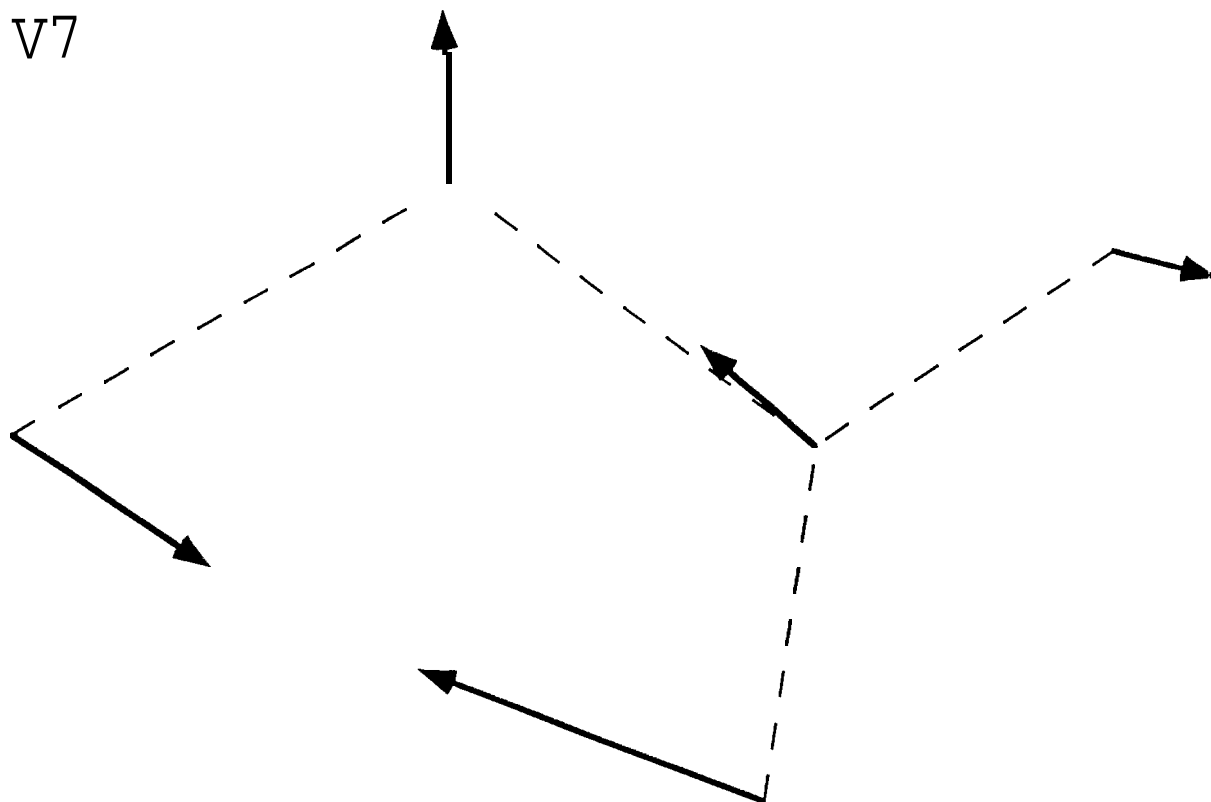
J. Pol. Sci.; 1974, vol. 1, p. 5



V_6

J. Pol. Spec.; Ruller et al.; Fig 5

V7



2. Pol. Spec ; Pukel et al. ; Fig 5